PROGRESS REPORT

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VACUUM U-V PHOTOLYSIS OF CARBON DIOXIDE

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Progress Report

The McBain-type quartz spring balance which was available in the laboratory and on which work was reported in the last Progress Report proved eventually to be insufficiently sensitive for the purpose of O-atom pick-up measurement anticipated in the CO_2 photolysis. A mass sorption balance commercially available from Worden Quartz Products Inc. was ordered, modified to the specifications required in our set-up. There was considerable delay in the actual manufacture but almost two months for the actual delivery. Eventually the shipment was located in California(!) and delivery achieved.

The fused quartz springs for maximum load of 0.10g have been calibrated with standard weights. The spring elongation as a function of weight has been found to be linear. It has also been established that no permanent stretching occurs even under maximum load for long periods of time. Using a large cathetometer to follow the spring elongation, the minimum weight change that is detectable is 10^{-3}mg with an accuracy of about $\pm$ 5percent. Since the minimum weight change expected from the adsorption of O-atoms during a CO_2 photolysis of 15 min. duration in a static system should be of the order of 10^{-2}mg, the spring balance should detect the expected change.

The problem of finding a suitable adsorbent, adsorbing O-atoms at room temperature, but not CO_2, is still in progress. It would be useless to recite the cases tested up to the present without success. The literature gives reference to the use of MoO_3 as a color indicator for qualitative estimation of the presence of O-atoms. The basis of

the reaction claimed is:

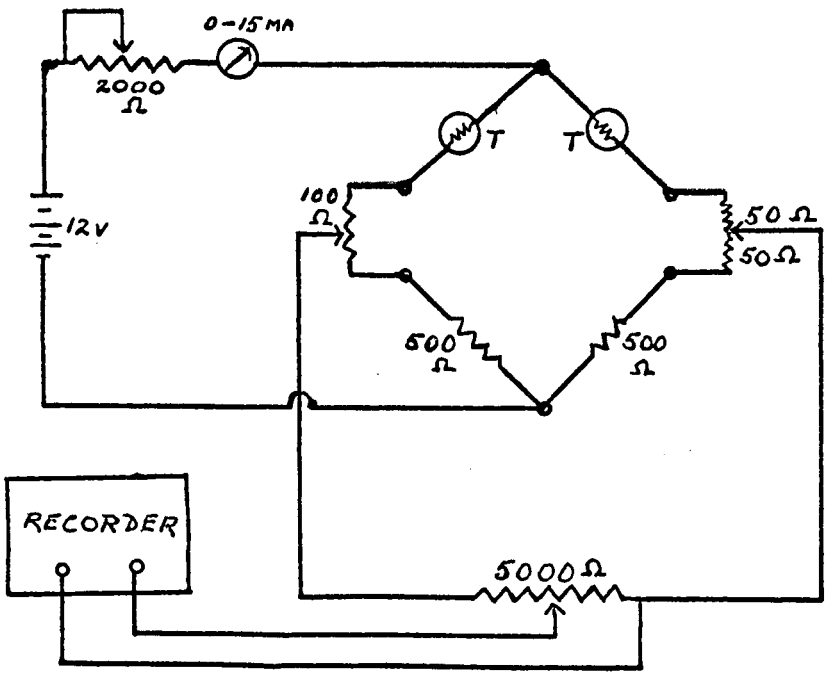
$$3\ MoO_3 + O = Mo_3O_8 + O_2$$

the color change being from the pink MoO_3 to blue Mo_3O_8. This reaction, even if valid, would not serve our present purpose. However, the numerous oxides of molybdenum suggest that a pure O-atom adsorption might occur and studies are in progress of any adsorption in (a) O_2, (b) CO_2, (c) irradiated O_2 containing O-atoms and (d) irradiated CO_2, as reflected in weight changes on the mass sorption balance suspended in the gases.

The determination of the production of CO from the CO_2 photolysis is to be made on the basis of the change in thermal conductance of the mixture, assuming that O-atoms are removable. To this end, a pair of thermistor beads, each mounted on a two terminal hermetic seal type header with 8000 ohms resistance, have been incorporated in a Wheatstone bridge circuit and hooked up to a 0 - 1mv recorder to provide continuous monitoring. The circuitry of the bridge is shown in the accompanying diagram. The photolysis system being a static one, calibration of known mixtures of CO and CO_2 must be made. With the present set-up, since the currents ($\sim$ 2ma) across the thermistors are sufficient to produce temperature changes and the heat conduction to the surroundings through pyrex glass is not very efficient, small differences in the temperature of the two thermistors have resulted in considerable drift of the bridge balance so that stable readings could not be achieved. By replacing the thermistor holders with massive metal ground joints to the reaction vessel and connecting

together with metal conductors to maintain both thermistor holders at the same temperature it is hoped to be able to stabilize the recorder tracings. As a last resort, the whole conductance gauge may have to be thermostatted. It is also possible that thermistors with a lower sensitivity and lower response could still have sufficient sensitivity for the required detection of changes in CO in the CO_2. It is along these lines that work is in progress but recorder stability is the prime requisite.

When the solution of these two major problems has been achieved the actual photolysis study can proceed quickly and the variation in CO_2 pressure, diluents, additives, as well as light intensity on the reaction investigated in detail.



Circuitry for Thermistor Cell 8K Pair